

D-20752-1

REMARKS

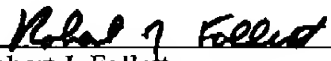
The specification and abstract page have been amended in accordance with the Examiner's comments.

Rejections under 35 USC 112:

The claims have been amended for clarity and to address the issues raised by the Examiner. No new matter has been introduced and the rejections are requested to be withdrawn.

In light of the above amendments and remarks, reconsideration of the pending application is requested.

Respectfully submitted,


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MARKED AMENDED SPECIFICATION

Page 1, first full paragraph:

This invention was made with government support under Contract No. DE-FC26-99FT40497 awarded by U. S. Department of Energy. The government has certain rights in the invention.

In the paragraph bridging pages 4-5:

M. Oba, et al. have reported in Journal of Polymer Science, Part A: Polymer Chemistry, Volume 34, pp 651, 1996; and in US Patent Nos. 5,753,407 and 5,756,650 that the imidization temperature of the polyamic acids can be lowered to about 150 ° C in the presence of large amount of catalysts (up to 2 equivalent per repeat unit of polyamic acid), such as *p*-hydroxybenzoic acid. The authors have not disclosed or implied that catalysts can be advantageously utilized to reduce imidization temperature of polyamic acid salts in membrane preparation. It is known in the art that polyimide polymers can be prepared from polyamic acid salt precursors, which are formed by neutralization of the free carboxylic acid group with a tertiary amine base. US Patents 4,290,929 and 5,719,253 disclose the use of polyamic acid solutions of tertiary amine. The following publications also disclose the synthesis of polyamic acid salts: R. J. W. Reynolds and J. D. Seddon, Journal of Polymer Science, Part C, Volume 23, pp45, 1968; and J. A. Kreuz, A. L. Endrey, F. P. Gay, and C. E. Sroog, Journal of Polymer Science, Part A-1, Volume 4, pp 2607, 1966; Y. Echigo, N. Miki, and I. Tomioka, Journal of Polymer Science, Polymer Chemistry, Volume 35, pp2493, 1997.

In the heading immediately before the fourth full paragraph of page 7, and in the fourth full paragraph of page 7:

List of Figures Brief Description of the Drawings

Figure 1 shows the effect of the catalyst on thermal imidization of triethylamine salt derived from polyamic acid formed from hexafluoroisopropylidene diphthalic anhydride and 4,4'-oxy-dianiline (6FDA-ODA/Et₃N) at different temperatures (catalyst 4-hydroxybenzoic acid, 10% by wt.).

In the paragraph bridging pages 7-8:

Figure 3 shows the effect of the catalyst on thermal imidization of triethylamine salt derived from polyamic acid formed from hexafluoroisopropylidene diphthalic anhydride and 4,4'-hexafluoroisopropylidenedianiline (6FDA-6FDA_n/Et₃N) at different temperatures (catalyst 4-hydroxybenzoic acid, 10% by wt.).

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In the paragraph bridging pages 12 and 13:

The hollow fiber configuration is a preferred membrane configuration for the polyimide membranes of the present invention because it allows for a high packing density of membrane area to be incorporated into a given volume. The porous polyimide hollow fibers of the present invention are prepared ~~from~~ from porous PAAS hollow fiber precursors that are produced by a dry-wet spinning process well known in the art. Such a process uses a solution, commonly referred to as a sol, a spinning dope, or spinning solution, comprising a polymer mixed with a solvent vehicle comprised of one or more components to yield a mixture with a viscosity suitable for hollow fiber spinning. The sol usually consists of at least one solvent capable of dissolving the polymer along with one or more additives that may be nonsolvents, as is well known in the art. The hollow fibers are prepared by spinning polymeric solutions through an evaporation zone, frequently referred to as air gap, followed by solidification in a coagulation media.

On page 16, first full paragraph:

The preferred composite membranes of the present invention are fabricated by the following process: (1) a coating solution of the PAAS precursor is formed in a solvent system that contains from 0.01% to 29% by volume ~~of~~ of tertiary amine or water; (2) the coating solution is applied to a porous substrate to form a coating layer; (3) the coating layer is solidified by drying or by immersing the coated substrate into a nonsolvent, in some embodiments a combination of drying and immersion into washing nonsolvent can be employed; (4) the solidified PAAS composite membrane is treated either by thermal or chemical means to convert it into a composite polyimide gas separation membrane. Coating applicators well known in the art can be utilized to apply PAAS polymer coating solution to the substrate. The coating layer can be solidified by drying, for example, by transporting the coated substrate through a drying oven. Alternatively the coating layer can be solidified by immersing the coated substrate into a nonsolvent, as described in US Patent 4,826,599. It is well understood that the solidification by immersion into a nonsolvent can be preceded by partial evaporation. In addition to solvents, the PAAS coating solutions can contain nonsolvents, surfactants and additives to promote optimal composite layer formation.

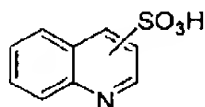
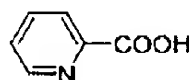
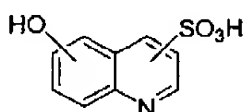
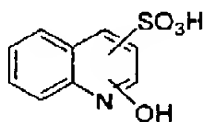
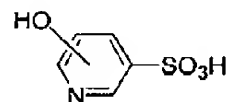
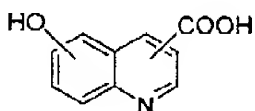
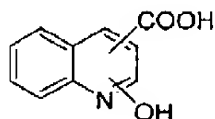
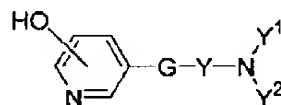
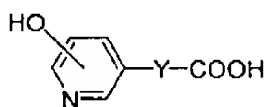
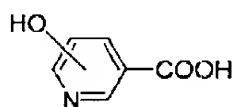
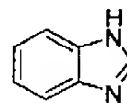
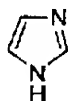
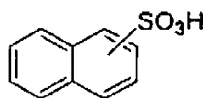
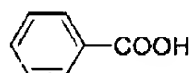
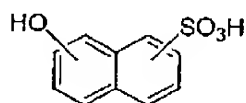
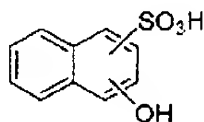
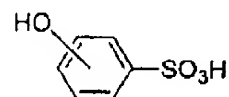
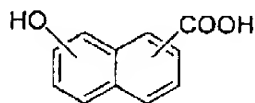
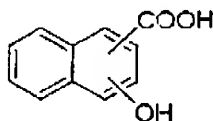
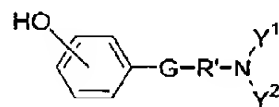
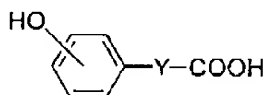
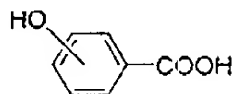
In the paragraph beginning on page 26 and ending on page 29:

In another aspect of present invention, it has been found that incorporating catalysts into the PAAS casting solution can lower the thermal imidization temperature of the PAAS articles, such as membranes. The weight ratio of the catalyst used to that of the PAAS polymer is in the range from 0.001:1 to up to 5:1, preferably in the range of 0.05:1 to 1:1. If the amount of catalyst used is too small, there will be no reduction in the thermal imidization temperature. If the amount of

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catalyst used is too large, the membrane formed can have inferior gas separation properties due to the presence of the residual catalyst. After the PAAS precursor is converted into the polyimide by thermal or chemical imidization, the catalyst can be optionally washed out with a solvent that does not effect the membrane adversely. Examples of preferred solvents include water, and alcohols. The catalyst is selected from one or several of the following compounds or oligomers containing the organic groups represented by the following formulas and derivatives thereof:

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where Y is an alkylene group having 1 to 10 carbon atoms, ethynylene group, G is $-C(=O)-O-$ or $-C(=O)-NH-$, and Y^1 and Y^2 are each a methyl group or an ethyl group. In preferred embodiments, the carboxylic and sulfonic groups of the catalyst are neutralized by a tertiary amine, such as triethylamine, tributylamine, or pyridine.

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The temperature utilized to convert the PAAS membrane precursor containing the catalyst into the polyimide membrane by heat treatment is in the range of 50 to 300°C, preferably in the range of 100 to 200°C. The preferred temperature will depend on the properties of the porous substrate and on the specific chemical structure of the PAAS polymer used. For the manufacturing of composite membrane, it would be advantageous to apply higher temperatures and short heating time when substrates with high glass transition temperatures are utilized. On the other hand, it would be advantageous to apply lower temperatures and long treatment times for substrates with low glass transition temperatures and thus obtain superior membranes with intact porosities. Heat treatments can be accomplished by microwave, radio frequency (RF) or infra-red heating, or by conveying the PAAS membrane precursors through a controlled temperature heating oven, preferably at a constant speed (the oven can contain several temperature zones), or by placing membranes into a heating oven and executing a controlled heat treating protocol. In some embodiments, a multi-step process that combines the heating procedures described above is advantageously employed. When the heat treating oven is employed, the heat treatment time can be in the range of 1 second to 100 hours, preferably from 0.1 minute to 30 hours, the length of the treatment being dependent on the temperature applied as well as on the PAAS polymer structure. Advantageously, a step-wise heating or temperature ramp-up process can be employed to avoid excessively fast release of the volatile species formed during the imidization reaction that can otherwise cause foam formation or produce large voids in the polyimide product. For example, the precursory PAAS is first treated at a relatively low temperature of about 100°C followed by a final heat treatment at about 150°. Some PAAS precursors may undergo degradation when heated in air at elevated temperatures. It is preferred that the heat treatment of such PAAS precursors is carried out in an inert gas atmosphere, such as a nitrogen atmosphere, or under vacuum. The rate of temperature increase during the heat treatment process can effect the gas permeation characteristics of the polyimide membrane. It was found that in some embodiments, it is advantageous to employ a high rate of temperature increase that can lead to improved fast gas permeance as long as excessive foaming and void formation is avoided. The preferred rate may depend on the particular PAAS polymer structure and membrane thickness, and can be determined by those skilled in the art through routine experimentation.

On page 35, last full paragraph:

Thermal imidization of 6FDA-ODA/Et₃N was carried out at 110 ° C, 120 ° C, 130 ° C and 150 ° C, respectively, with or without the presence of the catalyst 4-hydroxybenzoic acid. Test films were cast on AgBr plates from a polyamic acid salt solution in methanol (concentration was about 4% by weight) in the presence or absence of a catalyst. The amount of catalyst used is specified in Figures 1- 5. FTIR spectra of treated films were obtained after heat treatment at a given temperature for a predetermined period of time. The degree of imidization was calculated by the

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method described by Delos et al. in Journal of Applied Polymer Science, Volume 27, 4295, 1982. The results are shown in Figures 1-2.

On Page 36, second full paragraph:

These thermal imidization examples demonstrate that the imidization temperature can be significantly lowered in the presence of catalysts. The thermal imidization rate increases as the amount of catalyst increases. The rate also increases as the thermal imidization temperature increases.

On page 27, first full paragraph:

A 0.25 % 6FDA-6FDAn/Bu₃N polymer solution in methanol was prepared. Porous polysulfone hollow fiber were coated by passing the hollow fiber through the PAAS polymer solution and ~~dried~~^{dyed}. The resulting composite membrane was placed into 1 % acetic anhydride cyclohexane solution for 72 h and air dried. The composite membrane was further overcoated with a solution of cross-linkable polysiloxane Sylgard 184, Dow Corning Co., 3.0 % by weight in cyclohexane. The gas permeation properties of the thus prepared membrane were measured at 50°C. The membrane exhibited a permeance of 3.32×10^{-5} cm³(stp)/cm²•cmHg•sec for oxygen and a permeance of 1.06×10^{-4} cm³(stp)/cm²•cmHg•sec for CO₂ combined with a gas separation factor of 4.3 for oxygen over nitrogen and a separation factor of 15.4 for CO₂ over CH₄.

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MARKED AMENDED ABSTRACT PAGE| ABSTRACT OF THE INVENTION-DISCLOSURE

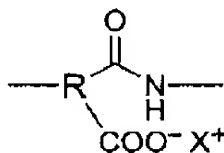
Soluble polyamic acid salt (PAAS) precursors comprised of tertiary and quaternary amines, ammonium cations, sulfonium cations, or phosphonium cations, are prepared and fabricated into membranes that are subsequently imidized and converted into rigid-rod polyimide articles, such as membranes with desirable gas separation properties. AMethod of enhancing solubility of PAAS polymers in alcohols is also disclosed.

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MARKED AMENDED CLAIMS

In the claims:

1. (Twice Amended) A polyimide article formed from a polyamic acid salt precursory article by thermal or chemical imidization, wherein said polyamic acid salt precursory article is formed from a casting solution containing from 0.01% to 20 % by volume of tertiary amines or water, wherein said polyamic acid salt precursory article contains the following radicals:



wherein R is a substituted or unsubstituted aromatic, alicyclic, heterocyclic, or aliphatic radical; and

X is an ammonium ion, a phosphonium ion, a sulfonium ion, a protonated tertiary amine or a quaternary amine or a mixture thereof.

3. (Once amended) The fluid separation membrane of claim 2 wherein said tertiary amine in said casting solution is the same as the protonated tertiary amine used to form the counter-ion X of said polyamic acid salt precursory article ~~polymer~~.

4. (Once amended) The fluid separation membrane of claim 2 wherein said tertiary amine in said casting solution is different from the protonated tertiary amine used to form the counter-ion X of said polyamic acid salt precursory article ~~polymer~~.

8. (Twice amended) A ~~polyamide-polyimide~~ fluid separation membrane wherein the polyimide membrane is a composite membrane formed by the following process: a) forming a coating solution of a polyamic acid salt polymer in a solvent system that contains from 0.01% to 20 % by volume of tertiary amine or water; b) applying said coating solution to a porous substrate to form a coated substrate; c) solidifying said coating solution by drying or by immersing said coated substrate into a non solvent; d) converting said coated substrate having the solidified coating into a final polyimide composite membrane by thermal or chemical treatment.